FUNDAMENTAL STUDY OF ADSORPTION OF HYDROCARBONS ON PLATINUM ELECTRODE

M.BONNEMAY, G.BRONOËL, D.DONIAT and J.P.PESANT

Laboratoire d'Electrolyse
du C. N. R. S.

I. INTRODUCTION.

The purpose of this report is to present the results obtained by a selective method of analysis of adsorption in connection with the study of the kinetics of fixation of hydrocarbons on smooth platinum. The principle involved and the experimental equipment used in this method have been described in a number of articles [1-2] and we will not go into them further at this time. However, we have considered it appropriate to emphasize the basic differences existing between the method used by us and those which were selected by other authors dealing with the same subject. These differences should in fact be kept in mind in comparing our results with those previously published.

II. BASIC CHARACTERISTICS OF THE SELECTIVE METHOD FOR THE STUDY OF ADSORPTION.

The study of adsorption processes is usually carried out from an analysis of the shape of the isothermal curves, that is to say the curves representing the variation of electrode coverage θ as a function of the concentration of substances in the medium under consideration. This method is not very appropriate when the concentrations are very weak, because all isothermal curves are practically straight in cases of low concentration. That is the case with hydrocarbons the solubility of which is rather low in aqueous solutions.

On the other hand, the analysis of curves representing the variation of the coverage as a function of adsorption time makes it easier to reveal and differentiate the various adsorption mechanisms involved, even for low concentrations. That is because the curve submitted to analysis always shows a well marked curvature, which facilitates identification by theoretical kinetic functions.

In connection with their research in adsorption kinetics, some authors have also resorted to the analysis of the coverage development curves as a function time. However, in all cases the standard procedures are characterized by the fact that the electrode is polarized during the adsorption phase and that the coulometric measurement of the coverage takes place in the medium containing the adsorbable substances. As for this last point, it can be admitted that the degree of error committed is small since the duration of the phase during which the coulometric measurement is effected is a very short part of the duration of the adsorption phase. But on the other hand, the presence of a faradic current causes more serious trouble. In fact, under these circumstances the total adsorption kinetic, that is to say the development of the electrode coverage, depends not only on the characteristic constants of the elementary processes of adsorption and desorption, but also on the constants characteristic of the charge transfer. In fact :

$$\frac{d\theta}{dt} = \vec{V} - \overleftarrow{V} - \frac{i}{nF} \qquad (1)$$

in which

$\frac{d\theta}{dt}$ is the coverage velocity of the electrode,

$\vec{V}$ and $\overleftarrow{V}$ are, respectively, the adsorption and desorption velocities, and

$\frac{i}{nF}$ is the faradic term.

The result is that the experimental curves characteristic of the variation of the coverage as a function of the adsorption time, obtained by these methods, depends on the value of the overall charge transfer terms which in turn depend on the overvoltage applied. Thus, the differences observed between the curves taken at more than one adsorption potential are difficult to exploit. Moreover, the passage of a faradic current, which is never a negligeable one, is accompanied by the formation of various reaction products the adsorption of which on the electrode and the chemical reactivity of which with the adsorbate may change considerably the adsorption kinetics under study.

A second disadvantage is linked with the fact that in the method generally used the kinetics of mass transfer actions and in particular of diffusion cannot always be considered rapid in relation to the phenomena under study. Therefore, the analysis of the curves representing the adsorption imply the consideration of a term characteristic of the diffusion processes and the necessity of a correction which it is usually difficult, if not impossible, to make.

III. BASIC EQUATION FOR THE ANALYSIS OF ADSORPTION KINETICS.

In heterogeneous catalysis, it is often found that the kinetics of adsorption obeys a law which can be expressed by the formula :

$$\frac{d\theta}{dt} = V_o \exp(- a\theta)$$

in which V_o is the initial adsorption velocity (for $\theta = 0$).

Most authors explain that this formula, called the Elovich equation [3], is obtained by a linear variation of the adsorption activation energy with the coverage. More than one hypothesis has been offered as to the origin of this variation of activation energy. Systems have been suggested implying heterogeneity of active sites without interaction between adsorbed molecules [4] or homogeneity of sites with interaction between the molecules of the adsorbate [5]. In this latter case, parameter a of equation (2) serves as a coefficient of interaction. More recently, a concept has been suggested [6] which implies the creation of energy chains on the surface of the solid.

Similar considerations have also been adopted to measure adsorption in an electrolytic medium and have led to various isothermal expressions [7-8]. However, in some cases, although the kinetics observed has the Elovich form, it is unlikely that a pronounced heterogeneity of the sites or interactions in the adsorbate should be expected. We therefore considered it wise to

see if other processes of reasoning, not presupposing a relationship between the adsorption activation energy and the coverage, would result in obtaining functions of the same form.

Let us consider first the case of non-dissociative adsorption of a compound on a surface so homogeneous that the reaction surface is the same as the apparent surface.

The general equation for the kinetics of adsorption is :

$$\frac{d\theta}{dt} = \frac{kT}{h} C\ (1-\theta)\ \exp(-\frac{W}{RT}) - \frac{kT}{h}\theta\ \exp(-\frac{W'}{RT}) \qquad (3)$$

in which:

k, T, h and R have their usual meanings,

C is the partial pressure of the active substance,

and W and W' are respectively the activation energies of adsorption and desorption.

For low coverages, it is possible to disregard the desorption term $\frac{kT}{h}\theta\ \exp(-\frac{W'}{RT})$.
We then have :

$$\frac{d\theta}{dt} = \frac{kT}{h} C\ (1-\theta)\ \exp(-\frac{W}{RT}) \qquad (4)$$

The term $(1-\theta)$ for $\theta \ll 1$, can be identified at the start of the development in series of $(\exp - \theta)$, which means that equation (4) is equivalent under these circumstances to :

$$\frac{d\theta}{dt} = \frac{kT}{h} C\ \exp(-\frac{W}{RT})\ \exp(-\theta) \qquad (5)$$

Consequently, we see in this case that the kinetics observed can be described by a law or formula analagous to equation (2), the term a then being equal to 1.

When, for a reaction of the same type, the reacting surface is composed of two fractions X_o and Y_o characterized by sites having different activation energies W_1 and W_2, we can write expressions analagous to equation (4) for X_o and Y_o.

Assuming :

$$\theta_x + \theta_y = \theta \qquad \text{et} \qquad \frac{d\theta_x}{dt} + \frac{d\theta_y}{dt} = \frac{d\theta}{dt}$$

we obtain by means of a development in limited series a fonction $\frac{d\theta}{dt} = f(t)$ of the form :

$$\frac{d\theta}{dt} = mX_o + nY_o - t(X_o m^2 + Y_o n^2) \qquad (6)$$

with: $m = \frac{kT}{h} C \exp(-\frac{W_1}{RT})$

and $n = \frac{kT}{h} C \exp(-\frac{W_2}{RT})$

Equation(2)expressed in the form $\frac{d\theta}{dt} = f(t)$ leads, with the same approximations, to :

$$\frac{d\theta}{dt} = V_o - V_o^2 \, a \, t \qquad (7)$$

Equation (6) can therefore be identified with equation (7), in which the term a has the following value :

$$a = \frac{X_o m^2 + Y_o n^2}{(X_o m + Y_o n)^2}$$

Similar treatment carried out for a surface which can be decomposed into n fractions also gives us, for $\frac{d\theta}{dt} = f(t)$, a formula which can be identified with equation (7).

It is easy to show that when $(W_2 - W_1) < 50$ cal., a tends toward 1, and the system acts substantially the same as in the case of a homogeneous surface. On the other hand, when $(W_2 - W_1) > 200$cal surface Y_o can be considered inactive and in that case a is equal to $\frac{1}{X}$ that is to say to the ratio of the apparent surface to the active surface.

Let us now consider the case of a dissociative adsorption produced on a surface the active fraction of which is X_o. The kinetics of the reaction :

$$AB + {}_{S}M \rightarrow AM_{S'} + BM_{(S-S')}$$

in which S is the number of sites occupied after adsorption of an AB molecule, can be written neglecting desorption :

$$\frac{d\theta}{dt} = \frac{kT}{h} C X_o \exp(-\frac{W}{RT}) \left[1 - \frac{\theta}{X_o} \right]^S \qquad (8)$$

or else, when $\frac{\theta}{X_o} << 1$:

$$\frac{d\theta}{dt} = \frac{kT}{h} C X_o \exp(-\frac{W}{RT}) \exp(-\frac{S}{X_o} \theta). \qquad (9)$$

This expression can be identified with equation (2) with $a = \frac{S}{X_o}$.

It is readily seen that many adsorption reactions have kinetics similar to that of Elovich without any phenomena of variation of adsorption activation energy being involved.

It is therefore absolutely necessary to take dissociation parameters and surface factors into account in order to evaluate the terms of any intermolecular interaction which may exist.

Equation (9) expresses effects of surface activity and of dissociation. It can be filled out to allow for a possible variation of adsorption activation energy. In that way we have a very general equation of the form [1] :

$$\frac{d\theta}{dt} = \frac{kT}{h} C X_o \exp(-\frac{W_o}{RT}) \exp(\frac{S + \alpha}{X_o} \theta) \qquad (10)$$

in which α represents the interaction coefficient and W_o is the initial adsorption activation energy.

The relationship must now be established between the experimental value q and the electrode coverage θ. θ is defined here as the proportion of the number of sites occupied by the adsorbed substances to the total number S_o of sites existing on the surface of the electrode. If S is the number of sites occupied after the adsorption of one hydrocarbon molecule (an adsorption which may have created other adsorbed particles by dissociation) and Z the number of electrons exchanged in the oxidation of the adsorbed molecule and its products of dissociation the relation between q and θ is written :

$$\theta = q \frac{N S}{Z F S_o} \qquad (11)$$

in which N is the Avogadro number and F the Faraday.

The quantity q is determined in such a way that it is exclusively a function of the oxidation or of the reduction of the adsorbate. Corrections should be made to eliminate any effects of double layer or of electrochemical transformation of the surface.

Combining equations (9) and (10), we obtain :

$$\text{Ln} \frac{dq}{dt} = \text{Ln}\left[\frac{kT}{h} C X_o \frac{Z F S_o}{N S} \exp\left(- \frac{W_o}{RT}\right)\right] - q \frac{N S}{Z F S_o} \left(\frac{S+\alpha}{X_o} \right) \qquad (12)$$

Plotting the $\frac{dq}{dt} = f(q)$ function in a semi-logarithmic form gives us a straight line the ordinate of which at point of origin L_o and the slope P_o are expressed, respectively, as follows :

$$L_o = \text{Ln}\left[\frac{kT}{h} C X_o \frac{Z F S_o}{N S} \exp\left(- \frac{W_o}{RT}\right) \right] \qquad (13)$$

$$P_o = \frac{N S}{Z F S_o} \left(\frac{S+\alpha}{X_o}\right) \qquad (14)$$

Generally speaking, four parameters are unknown : X_o, S, W_o and α. When parameters X_o and S are constant within a given temperature range, an examination of the variation of L_o as a function of T enables us to know the value of W_o.

Knowledge of an additional factor is then necessary in order to determine the other parameters on the basis of equations (13) and (14). This additional factor may be relative to X_o or to the parameter S. Measurements of the double layer differential capacity generally enable us to obtain information on these parameters. As regards S, it is possible to relate the double layer capacity C_d to θ [9] in the following way :

$$C_d = C\theta + C'(1-\theta) \qquad (15)$$

in which C and C' are the specific capacities of the surface whether covered or not. Continuing equations (11) and (15) we obtain the additional factor of relationship which was sought between C_d, q and S.

We find therefore that it is possible in this way to determine the characteristic values of an adsorption kinetic by resorting to only a minimum of assumptions.

IV. RESULTS.

This research was carried out on five alkanes (CH_4, C_2H_6, C_3H_8, n-C_4H_{10} and iso-C_4H_{10}), three alkenes (C_2H_4, C_3H_6 and n-C_4H_8) and on acetylene. The temperatures for the tests were fixed at 80°C and 90°C. The electrolyte medium was constituted by a normal solution of sulphuric acid or phosphoric acid. The electrode was a polished platinum plate. Before each phase of adsorption, this electrode was subjected to an electrochemical treatment [10] the purpose of which was to ensure perfect reproductibility of the surface condition of the metal.

For each hydrocarbon under the conditions stated above, we obtained the q=f(t) curves representing, according to the adsorption time t the quantity of electricity corresponding to the oxidation of the adsorbed substances.

The functions Ln dq/dt = f(q) were plotted on the basis of the q=f(t) curves. Some interesting features of regularity appeared in this form of expression. By way of example, the curves obtained from the tests made in H_2SO_4 N at 80°C are shown in figure 1.

Exploitation of these curves and of the differential capacity measurements enable us to determine the constants characteristic of the adsorption kinetics involved. Moreover, the special behavior of methane enabled us to make a separate calculation of these parameters. In fact, the stability of the methane molecule entails identical dehydrogenation at 80°C and at 90°C, which is confirmed by the identical slopes of the Ln dq/dt = f(q) curves plotted at both of these temperatures. $W_{o(80°)}$ is therefore equal to $W_{o(90°)}$ in the case of CH_4 and it is possible to compute its value from the ratio of the initial adsorption velocities.

The values of the parameters thus determined are shown in tables I, II and III.

V. DISCUSSION.

An examination of the results enables us to formulate a number of remarks concerning the reaction mechanism involved in the course of the deposit of hydrocarbons on platinum.

It can be noted that in all the cases studied, with the exception of isobutane, the number of sites occupied by the products resulting from the adsorption of a molecule is equal to the number of carbon atoms contained in the molecule plus two. It can be assumed that the adsorption is dissociative and causes a break of C-H bonds in such a way that two hydrogen atoms are released, which occupy two sites. The carbon radical resulting from this dissociation is deposited on a number of sites equal to the number of carbon atoms which it contains.

This preferential dissociation involving the C-H bonds has already been suggested by various authors.

In the case of the alkanes and the ethylenes, as in the case of acetylene, the dehydrogenation probably occurs in the end groups of the chain. This assumption is also supported by the fact that the deposit of one molecule of isobutane results in the occupation of 7 sites. In fact, the presence in the molecule of this reactive agent of an extra methyl group appears to cause the break up of a third C-H bond.

This rate of site occupation does not necessarily indicate that each occupied site comprises a link with an adsorbed particle. Our examination of the very slight variation of W_o as a function of the number of carbon atoms contained in the molecules of hydrocarbons of the same series suggests rather that the number of bondings between the products of dissociation and the platinum remains constant. These bondings take place both between the platinum and the dehydrogenated end groups and between the platinum and the hydrogen atoms resulting from that dissociation. The other sites occupied are not linked but simply covered by the middle part of the chain.

It is worthy of note that the values found for S agree with the theoretical expectations and are different from those heretofore determined by chemical methods /11/.

In the final analysis, we are inclined to suggest a reaction system which includes as the final stage of the reaction occurring at zero current the formation of both adsorbed H and a C_xH_y radical comprising bondings with the platinum. However, it must be pointed out that if this radical reacts with its environment (O or OH compounds, for example), the number of sites occupied may then be the same as for the C_xH_y radical alone. The suggested system therefore constitutes only one of the possible solutions for a given number of sites.

It should also be stressed that, under the assumption of adsorption accompanied by chemical reactions leading to partial oxidation of the C_xH_y radical, the coulometric measurement will not depend at all on the state of oxidation. In fact, if the anodic pulse causes the formation of CO_2 and H_2O, the number of coulombs will always be the same regardless of the state of oxidation of the substance adsorbed to the extent that this oxidation can only involved the oxygen derived from the water or anions of the acid.

A number of observations can also be made in regard to the values found for the coefficient α. Actually, for a given medium and temperature, this coefficient increases as a function of the length of the molecule adsorbed. Moreover, α is subject to a decided increase when, in the case of molecules having the same number of carbon atoms, the number of radicals undergoing a breakage of bond increases. This would seem to indicate that the greater the separation of the end groups the smaller will be the intramolecular interactions and the larger the term α when measured.

Coefficient α is usually lower for an ethylene hydrocarbon than for a saturated hydrocarbon, with the same number of carbon atoms and an identical degree of dissociation. It is also observed that acetylene shows a very high interaction coefficient. This probably has to do with the fact that the dehydrogenation of this compound produces a highly reactive carbon containing residue which may react on the environmental medium.

Attention should be called to the fact, however, that even with the highest values of the interaction coefficient α, the variations of the adsorption activation energy W as a function of the coverage remain comparatively low. In fact, in the case of isobutane, a reactive agent which involves the strongest interaction, the variation of W is about 620 cal/mole while the coverage increases from 0 to 0.1 (which was the case in our experiments).

As regards the effect of the nature of the electrolyte on the value of coefficient α, the results obtained indicate a decided variation of this parameter according to whether the medium is sulphuric or phosphoric acid. This interaction coefficient is therefore not only linked with forces of attraction or repulsion between adsorbed molecules but also with the action of the ions of the electrolyte. It is probable that the effect of the anions is dominant, which would be in full agreement with the specific adsorption of H_3PO_4 ions brought out in other articles on the subject /12-13/.

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TABLE I

Hydrocarbon	z	S	W_o cal/mole	α
CH_4	8	2,1	22 500	11
C_2H_6	14	3,9	23 300	0,94
C_3H_8	20	4,7	23 200	3,80
$n.C_4H_{10}$	26	5,6	22 900	5,59
$iso.C_4H_{10}$	26	6,6	23 200	8,85
C_2H_4	12	3,8	22 300	1,34
C_3H_6	18	4,7	21 700	3;38
$n.C_4H_8$	24	5,7		4,22
C_2H_2	10	3,9	22 400	5,81

in H_2SO_4 at 80°C

TABLE II

Hydrocarbon	z	S	W_o cal/mole	α
CH_4	8	2,1	22 500	11
C_2H_6	14	4,2	23 300	1,66
C_3H_8	20	5,1	23 100	3,91
$n.C_4H_{10}$	26	6,1	22 900	9,99
C_2H_4	12	4,1	21 900	4,29
C_3H_6	18	5,1	21 200	5,87
$n.C_4H_8$	24	6,15		9,08
C_2H_2	10	4,2	21 300	5,14

in H_2SO_4 at 90°C

TABLEAU III

Hydrocarbon	z	S	W_o cal/mole	α
CH_4	8	1,9	22 400	15
C_2H_6	14	3,7	22 100	7,6
C_3H_8	20	4,6	22 000	13,9
C_2H_4	12	3,6	21 500	5,6
C_3H_6	18	4,6	21 000	12,1
C_2H_2	10	3,8	19 200	11,9

in H_3PO_4 at 80°C

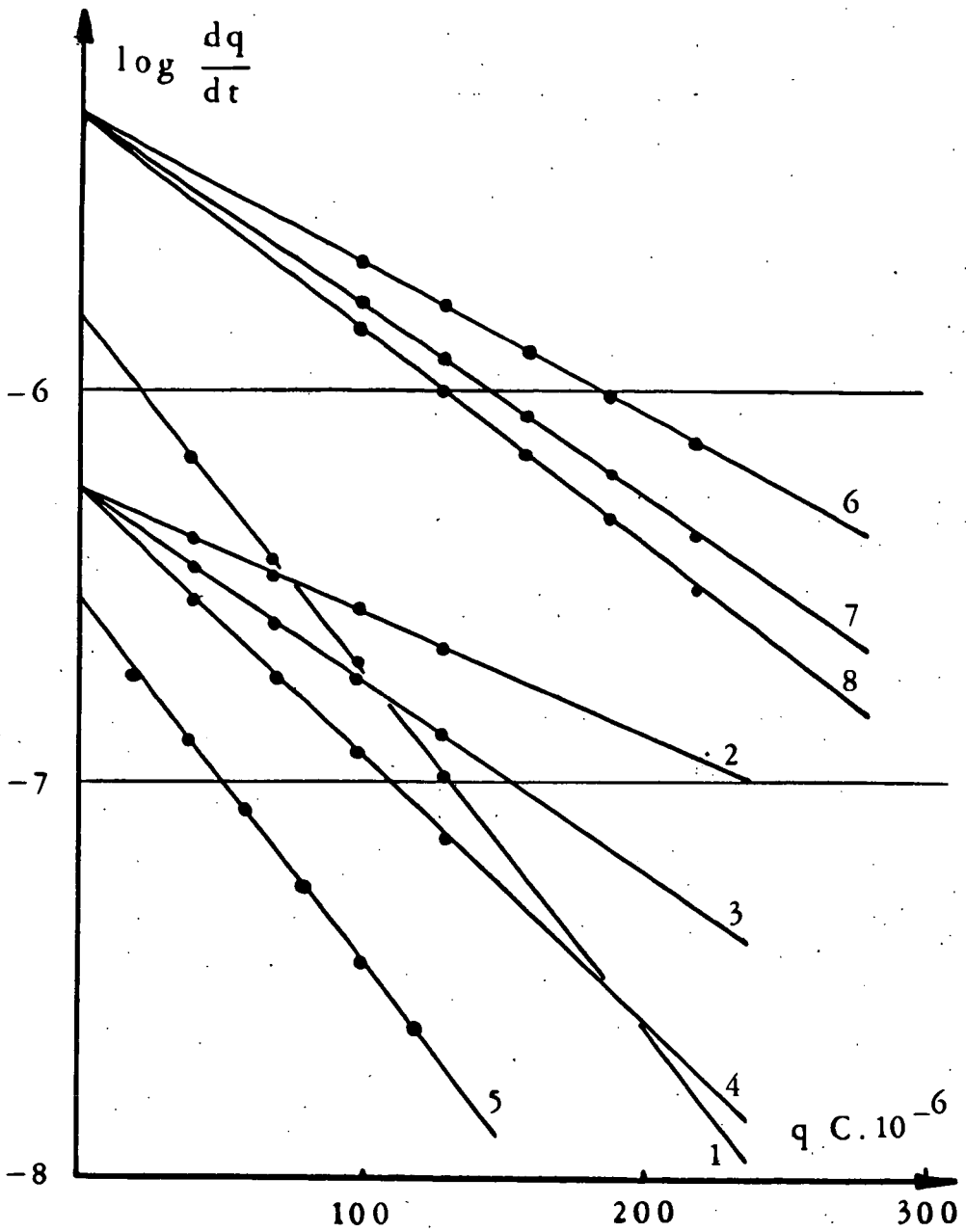

FIGURE 1 Plots of $\log_{10}$ dq/dt versus q in H_2SO_4 N medium at 80°C for :

1- CH_4; 2-C_2H_6; 3-C_3H_8; 4- n.C_4H_{10}; 5-iso-C_4H_{10};

6-C_2H_4; 7-C_3H_6; 8- n.C_4H_8.